The Equilibrium between Arsenious Acid and Iodine in Aqueous Solution

By EARLE KENNETH STRACHAN

B. S. WORCESTER POLYTECHNIC INSTITUTE, 1908
M. S. UNIVERSITY OF ILLINOIS, 1910

THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS

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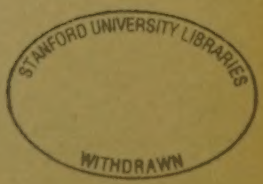

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1. Purpose of the Investigation.

When by dilution the mol fraction of the solute molecules in any solution becomes so small that the thermodynamic environment[1] prevailing within the solution is substantially determined by the nature of the solvent molecules and is not appreciably affected by further dilution, then the solution may be classed as a "dilute" solution and will, within the experimental error, be governed by that set of limiting laws which are called, the Laws of Dilute Solutions. Solutions for which this condition is not fulfilled will exhibit deviations from these laws of magnitudes varying with the natures of the solute and solvent and with the degree of dilution. The development of a satisfactory theory for interpreting the behavior of this second class of solutions constitutes the problem of "concentrated" solutions in the sense in which the term is used in this paper.

The behavior of solutions of strong electrolytes in water indicates that the change of thermodynamic environment with changing concentration persists up to much higher dilutions than is the case with aqueous solutions of other solutes. In fact, it seems to persist up to such high dilutions in many instances that, before a point is reached where it becomes approximately constant, the experimental errors in the data concerning the solutions have become so large that it is no longer possible to draw trustworthy conclusions from them. This is illustrated, for example, by the familiar behavior of the strong electrolytes toward the law of mass action.

With respect to this behavior, however, most of the attention in the past has been directed to the application of this law to the simple process of the dissociation of a strong electrolyte into its ions, and very little *exact*

[1] *Trans. Amer. Electrochem. Soc.*, 22, 331 (1912); 21, 125 (1912).

study has been made of other types of chemical reactions involving the ions of the strong electrolytes. The work which has been done in this field shows, it is true, that the other types of reactions thus far investigated do not exhibit the large deviations from the law of mass action which characterize the simple ionization process, but the limits of error in most of the investigations thus far made, have been comparatively large and very decided deviations from the mass action law might still be present without being detected. As an example of this may be cited the work of Victor Sammet[1] which is one of the most thorough and accurate investigations of such a reaction that has been made.

Sammet investigated the equilibrium of the reaction,

$$6H^+ + 5I^- + IO_3^- = 3I_2 + 3H_2O.$$

He varied the concentrations of the different reacting substances through rather wide limits and was unable to find any evidence indicating a deviation from the law of mass action. For example, as the mean of one series of determinations of the equilibrium constant of this reaction, he found $K = 0.26.10^{-46}$ while another set yielded the value $K = 0.46.10^{-46}$. The second value is nearly double the first and individual experiments show even greater differences. As Sammet, himself, states,[2] however, the agreement is as good as could be expected considering the uncertainty in the values of some of the auxiliary data employed in the calculation, and cannot be taken as indicating any real deviation from the requirements of the law of mass action.

Another equilibrium of this character which has been investigated is that between arsenious acid and iodine as expressed by the equation

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^-.$$

This reaction has been studied by J. R. Roebuck,[3] but the value of the equilibrium constant computed from his data is so uncertain, owing to the errors from various sources, that we can only conclude that at least no very great deviation from the law of mass action is indicated. Roebuck's experiments, however, showed that a definit equilibrium is quickly and easily reached and made it appear probable that the adoption of different experimental methods and the careful measurement of all the auxiliary data required would make it possible to compute the value of the equilibrium constant of this reaction with such a degree of accuracy that the total uncertainty in it, due to the combined effects of all the errors in the separate data required, would not exceed 10%. Any variation from the requirements of the mass action law which exceeded this amount might, therefore, be detected.

[1] Sammet, *Z. physik. Chem.*, **53**, 656 (1905).

[2] *Loc. cit.*,

[3] Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905).

In addition to the general theoretical interest attached to a more exact study of such an equilibrium, this particular equilibrium is also interesting because of the fact that it lies at the foundation of what is perhaps the most accurate method of titrametric analysis known, the determination of iodine by titration with a standard solution of arsenious acid.[1] The development of this analytical method affords a striking example of the value of the ionic theory in the field of quantitative analysis, for it is owing to this theory that it was possible to secure that insight into the equilibria involved in the method which made it possible to recognize and to eliminate its sources of error and to predict those modifications which were necessary in order to give it the great exactness which it now possesses. By means of this method the atomic weight ratio, As_2O_3/I, and through it the atomic weight of arsenic could probably be determined with an accuracy of a few thousandths of one per cent. When employed in conjunction with the iodine coulometer the method, moreover, makes possible the determination of the exact value of the faraday with a degree of certainty unattained by any other coulometer.[2]

2. Previous Investigations.

In the investigation by J. R. Roebuck, referred to above, the following experimental method was employed: Measured quantities of standard solutions of sodium arsenite (As_2O_3 dissolved in $NaHCO_3$), iodine, potassium iodide, and sulfuric (or hydriodic) acid were mixed with water and allowed to come to equilibrium in a stoppered bottle at 0°. When equilibrium was attained a sample was withdrawn, diluted with ice water in order to decrease the rate of reaction, and then the "free" iodine titrated with standard thiosulfate solution. This titration was carried out as rapidly as possible, since the removal of the "free" iodine present disturbed the position of the equilibrium and caused an additional quantity to be formed. From these data an equilibrium constant was calculated.

The chief sources of error inherent in this experimental method are, as Roebuck, himself, points out; (1) The error due to the disturbance of the equilibrium in the process of determining its position, and (2) the formation of some "free" iodine by the action of dissolved oxygen according to the reaction,

$$O_2 + 4H^+ + 4I^- = 2I_2 + 2H_2O.$$

Aside from the influences of these sources of error, the use of Roebuck's data in order to calculate the true equilibrium constant of this reaction with any degree of certainty is rendered still more difficult by the fact that sodium and potassium salts, carbonates and bicarbonates, and in many experiments sulfuric acid also, were present in the equilibrium mixture. The presence of these additional substances greatly compli-

[1] Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908).

[2] Washburn and Bates, *Ibid.*, **34**, 1341 (1912).

cates the calculation of the concentrations of the molecular species directly concerned in the equilibrium itself and consequently introduces considerable uncertainty into the computation of the true equilibrium constant.

Roebuck, in fact, made no attempt to compute the true equilibrium constant, but contented himself with expressing his results in a form equivalent to the following:

$$\frac{[\text{As}'][\text{free acid}]^2[\text{iodide}]^3}{[\text{As}][\text{tri-iodide}]} = const., \qquad (1)$$

where each quantity in brackets signifies the *total* concentration of the material indicated, in all the forms in which it is present in the solution. Thus [As′] indicates $[H_3AsO_4] + [H_2AsO_4^-] + [NaH_2AsO_4] + [KH_2AsO_4]$, and [tri-iodide] indicates $[HI_3] + [I_3^-] + [NaI_3] + [KI_3] + [I_2]$, and similarly for the other substances involved.

The values of the "*const.*" thus calculated varied between the limits $1.03.10^{-5}$ and $0.364.10^{-5}$ in different experiments.[1]

An attempt to compute the true equilibrium constant from what seemed to be the most accurate as well as the simplest experiment carried out by Roebuck led to the value

$$\frac{[H_3AsO_4].[H^+]^2.[I^-]^3}{[H_3AsO_3].[I_3^-]} = 7.10^{-2} \text{ (approx.) for } 25°.^2 \qquad (2)$$

With the exception of an attempt by Loimaranta to measure directly the potential of the arsenic electrode, Roebuck's investigation is the only study of this equilibrium which had been made when the present investigation was undertaken. Loimaranta's experiments will be referred to below, section 14.

3. Outline of the Experimental Method.

The sources of error and uncertainty described above can be avoided by employing the following procedure: A standard solution of pure arsenious acid dissolved in air-free water is allowed to react, out of contact with the air, with a second non-miscible phase containing a suitable quantity of pure iodine. The other substances concerned in the equilibrium should be insoluble in this second phase, which for convenience may be called the *reference phase*. Under these conditions the reaction which occurs may be written

$$H_3AsO_3 + 2H_2O + I_2 = H_3AsO_4 + 2H^+ + 2I^-.$$

Immediately, however, the iodide ions produced react with more of the molecular iodine according to the reaction

$$I^- + I_2 = I_3^-$$

to give tri-iodide ions and when equilibrium is finally attained nearly all of the "free" (*i. e.*, titratable) iodine present in the solution exists in the

[1] *Loc. cit.*, Table XXXVIII, p. 763 of Roebuck's second paper.

[2] Washburn, *loc. cit.*, 34.

form of tri-iodide. The equation for the equilibrium may, therefore, be conveniently written

$$H_3AsO_3 + 2H_2O + I_3^- = H_3AsO_4 + 2H^+ + 3I^-.$$

As will be shown later, when this equilibrium is attained, the solution contains, in addition to water, only the following ten molecular species at appreciable concentrations: H_3AsO_3(or AsO.OH in acid solution), AsO^+, H_3AsO_4, $H_2AsO_4^-$, H^+, I_2, HI, HI_3, I^-, and I_3^-.

Now if the *total* arsenic concentration, ΣAs gram atoms per liter, the *total* iodine concentration, ΣI gram atoms per liter, and the concentration of molecular iodine, $[I_2]$, in the solution be determined, the concentration of each of the molecular species present can be computed in the following manner:

$$[\Sigma As] = [H_3AsO_3] + [AsO^+] + [H_3AsO_4] + [H_2AsO_4^-] \quad (3)$$

and

$$[\Sigma I] = 2[I_2] + [HI] + [I^-] + 3[HI_3] + 3[I_3^-] \quad (4)$$

Moreover

$$\frac{[I_2][I^-]}{[I_3^-]} = k_1 \quad (5)$$

and, as will be proved below, hydriodic acid, HI, and hydrotriiodic acid, HI_3, are ionized to the same degree, γ. Hence by combining equations (4) and (5) we have

$$[\Sigma I] - 2[I_2] = \frac{1}{\gamma}[I^-] + \frac{3[I_2][I^-]}{\gamma k_1}. \quad (6)$$

The value of $[I_2]$, the concentration of molecular iodine in the solution, may be calculated from its concentration in the reference phase and the distribution ratio between the two phases. Equation (6) gives us, therefore, at once the value of $[I^-]$. The values of [HI], $[HI_3]$ and $[I_3^-]$ can now be obtained from the equations,

$$[HI] = \frac{1-\gamma}{\gamma}[I^-] \quad (7)$$

$$[I_3^-] = \frac{[I_2][I^-]}{k_1} \quad (8)$$

$$[HI_3] = \frac{1-\gamma}{\gamma}[I_3^-]. \quad (9)$$

Now as all the iodide, both ionized and unionized, results from the oxidation of arsenious acid, whereby for every molecule of arsenic acid formed, two molecules of hydriodic acid are obtained, and as all the triiodide results from the reaction, $I^- + I_2 = I_3^-$, it follows that the sum of all the molecules of hydriodic acid and of hydrotriiodic acid is twice the total number of molecules of arsenic acid, or

$$2[H_3AsO_4] + 2[H_2AsO_4^-] = [HI] + [HI_3] + [I^-] + [I_3^-]. \quad (10)$$

In order to obtain $[H_3AsO_4]$, use is made of the ionization constant of arsenic acid,

$$\frac{[H_2AsO_4^-][H^+]}{[H_3AsO_4]} = k_{As'}, \qquad (11)$$

the hydrogen ion concentration being obtained by a method of successive approximations to be explained below. The value of $[H_3AsO_3]$ can be obtained from equation (3) together with the equilibrium relation

$$\frac{[AsO^+][OH^-]}{[H_3AsO_3]} = k_{As}. \qquad (12)$$

As the reference phase an excess of pure solid iodine was employed in the initial experiment. Under these conditions the value of $[I_2]$ in the solution is equal to the solubility of iodine in water. It was found, however, that when the equilibrium is established in the presence of an excess of iodine as a solid phase the reaction runs so far to the right that if the arsenious acid is to remain at a measurable concentration, the hydrogen ion concentration will rise to about 0.2 normal, which is rather undesirable. In order to avoid this and to make it possible to vary at will the value of $[I_2]$ in the solution, carbon tetrachloride was employed as the reference phase, preliminary experiments having shown that none of the other substances concerned in the equilibrium were appreciably soluble in this liquid.

The calculation of the equilibrium constant from the data obtained by this method evidently requires the knowledge of a number of auxiliary data in the way of equilibrium constants and degrees of ionization, several of which had to be especially determined for this investigation. After the methods of purification of materials and preparation of solutions have been given, the determination of these auxiliary data will be described, before the experiments dealing directly with the arsenious acid-iodine equilibrium itself are taken up.

4. Purification of Materials and Preparation of Stock Solutions.

Arsenious Acid.—Kahlbaum's Ph.G.IV, arsenic trioxide was crystallized once from hydrochloric acid and twice from conductivity water. After the first crystallization from water the substance went into solution completely, leaving no residue. The following method was used in making up the solution for the equilibrium determinations. The desired amount of conductivity water was collected, boiling hot, from the still, and at once sufficient arsenic trioxide to make a 0.05 molal solution was added to it. The water was then boiled until the arsenic trioxide had completely dissolved. While still hot the solution was transferred to a bottle of resistance glass. This bottle was fitted with a rubber stopper through which two glass tubes passed, one of them reaching just through the stopper, and the other to the bottom of the bottle. As soon as the solution had been

introduced into the bottle, the longer tube was stopped and the shorter one connected to a supply of nitrogen gas. In this way the solution was allowed to cool and was then preserved out of contact with the air. By attaching the short tube to the gasometer containing the nitrogen, opening the long tube, and increasing the pressure on the nitrogen, the arsenious acid could be forced out of the bottle in any amount desired. The exact strength of the solution was determined by titrating it against pure iodine.

Arsenic Acid. This was prepared from the arsenic trioxide by evaporating it to dryness with a large excess of aqua regia. The residue was then taken up in pure water and evaporated to dryness several times, and was finally dissolved in enough conductivity water to make a twice molal solution. The exact strength of the solution was determined by precipitating the arsenic as magnesium ammonium arsenate.

Iodine. Kahlbaum's resublimed iodine was ground with some potassium iodide and sublimed. The resulting product was then resublimed without the addition of potassium iodide.

Hydriodic Acid. This was prepared by reduction of iodine with hydrogen sulfide, and subsequent distillation. After several distillations, the distillate was very pale yellow, and was free from sulfur.

Carbon Tetrachloride. Kahlbaum's carbon tetrachloride was saturated with iodine and allowed to stand over night. The iodine was then removed by shaking with a solution of sodium thiosulfate, and the carbon tetrachloride washed several times with conductivity water. It was finally distilled in a current of nitrogen, and the distillate preserved under nitrogen.

Nitrogen. This was prepared by passing dry air over hot granulated copper.

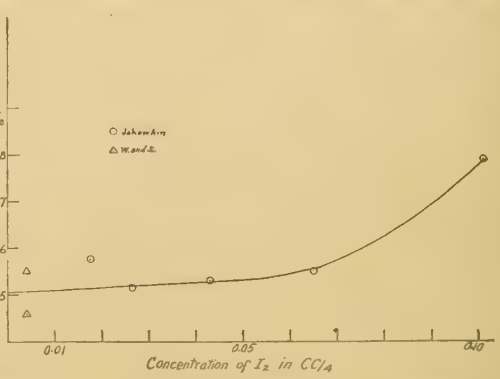
5. The Distribution of Iodine between Water and Carbon Tetrachloride.

Jakowkin[1] has determined the partition constant for this distribution at 25°, and has found that it decreases with decreasing concentration. For the purposes of this investigation, the partition constant must be known with a fair degree of accuracy, since an error in it of 1% causes an error of 4% in the equilibrium constant. Jakowkin's values, when plotted graphically (see figure) seem to indicate a decided increase in the partition constant at the lowest concentration measured by him. This is not what would be expected from theory. Moreover, as his investigations were carried out at considerably higher concentrations than those used in this work, it was thought desirable to make determinations of the partition constant at the concentrations actually used.

For this purpose, an accurately known weight of iodine was placed in a resistance-glass bottle together with an accurately known volume of water (10 liters) and of carbon tetrachloride (1 liter). An amount of sulphuric

[1] Jakowkin, *Z. physik. Chem.*, 18, 592 (1895).

acid (5 cc. of 1.84 sp. gr. acid) sufficient to prevent hydrolysis of the iodine, as calculated from the relation[1] $\frac{[HIO][I^-][H^+]}{[I_2]} = 0.3 \times 10^{-12}$, was added to the water. The mixture was then shaken at 25° until equilibrium was established, after which the carbon tetrachloride layer was pipetted off and analyzed. The total iodine used minus the amount of iodine in the carbon tetrachloride layer gave the amount of iodine in the water and thus the partition constant could be calculated. Two experiments gave for the ratio of the concentration of the iodine in the carbon tetrachloride to that in the water the values 85.6 and 84.7, respectively, when the iodine in the water layer was 5×10^{-5} mols per liter. The mean of these two agrees very well with Jakowkin's data, if the value he obtained at the lowest concentration be omitted, as will be seen by an examination of the figure.



6. The Conductance and Degree of Ionization of Hydriodic Acid.

The Conductance Data.—Ostwald[2] has determined the conductances of aqueous solutions of hydriodic acid at 25°, but as the recent work of Bray and Hunt[3] has shown that Ostwald's data for hydrochloric acid are in error by about 3%, it was thought best to measure the conductances of hydriodic acid solutions at those concentrations at which it occurred in the equilibrium mixtures.

The solutions employed for this purpose were obtained from the stock solution by shaking it with pure benzene until a colorless solution was obtained. These solutions were then analyzed and they remained colorless until the conductance measurements were completed. The conductance cells and other apparatus employed in these measurements have been described in a previous publication[4] from this laboratory. The results obtained are recorded in Table I. Columns I and II give, respectively,

[1] Bray, *J. Am. Chem. Soc.*, **32**, 932 (1910).

[2] Ostwald, *J. prakt. Chem.*, **32**, 302 (1885).

[3] Bray and Hunt, *J. Am. Chem. Soc.*, **33**, 786 (1911). For example, these investigators give 390.4 as the equivalent conductance of 0.1 normal HCl, while Ostwald found 381.0.

[4] Washburn and MacInnes, *Ibid.*, **33**, 1689 (1911).

the concentrations given by analysis and the measured equivalent conductances. Columns III and IV give the corresponding values for round concentrations as determined by graphical interpolation.[1]

TABLE I.—CONDUCTANCE AND IONIZATION OF HI AT 25°. CONCENTRATIONS IN EQUIVALENTS PER LITER. 1912 ATOMIC WEIGHTS.

I. C.	II. Λ.	III. C.	IV. Λ.	V. γ.	VI. η/η_0.
0.1710	386.8	0.1500	389.5	0.896	0.996
0.1028	395.0	0.1000	395.6	0.903	0.997
0.09020	397.7	0.0800	398.5	0.911	0.997
0.05140	403.7	0.0500	404.3	0.924	0.998

Calculation of γ. If Λ_I is the equivalent conductance of the total *iodide* (both ionized and unionized) in any solution of hydriodic acid and Λ'_{I^-} is the equivalent conductance of the *iodide ion* in the same solution, then the degree of ionization γ is given by the relation $\gamma = \Lambda_I / \Lambda'_{I^-}$. Concerning the correctness of this relation there can, of course, be no question. The question arises when we consider the method to be employed in evaluating the two quantities Λ_I and Λ'_{I^-}. The first of these can in all probability be correctly calculated by means of the relation

$$\Lambda_I = T_I \Lambda \qquad (13)$$

in which T_I is the transference number of the iodide ion-constituent and Λ the equivalent conductance of the HI, both at the concentration C.

The correct method for calculating Λ'_{I^-} is less certain. The general question involved here has been discussed by Washburn.[2] For the present we will simply state that the values of Λ'_{I^-} required for the purposes of the present paper have been obtained by employing the relation[2]

$$\Lambda'_{I^-} = \Lambda_{I^-} (f/f_0)^m \qquad (14)$$

in which Λ_{I^-} is the equivalent conductance of the iodide ion at zero concentration, (f/f_0) is the relative fluidity of the hydriodic acid solution for which γ is desired and m is the fluidity exponent for the iodide ion.

Combining equations (13) and (14) with the relation $\gamma = \Lambda_I / \Lambda'_{I^-}$, we have finally for the degree of ionization of hydriodic acid

$$\gamma = \frac{\Lambda}{\Lambda_{I^-}/T_I} \left(\frac{\eta}{\eta_0}\right)^m \qquad (15)$$

in which (η/η_0) is the relative viscosity of the solution. For the con-

[1] Ostwald's values are considerably lower than these. Thus for 0.1 normal HI he found $\Lambda = 386$.

[2] *Loc. cit.*, 133. In this article the evidence favoring the use of the relation $\Lambda'_{I^-} = \Lambda_{I^-} (f/f_0)^m$ has been set forth. See also the recent paper by Lewis, *J. Am. Chem. Soc.*, **34**, 1637 (1912), where a different point of view is taken.

centration range involved in this investigation (0.05 to 0.15 N) the value of T_I is practically constant and equal to 0.174. The value of Λ_1 at 25° is 76.5[1] and that of m is 0.8 but for the viscosities involved in this investigation may without appreciable error be taken as unity.[2] Equation (15) becomes therefore

$$\gamma = \frac{\Lambda}{440}\frac{\eta}{\eta_0} \quad \text{or} \quad \frac{\Lambda}{440/(\eta/\eta_0)}. \tag{16}$$

Column V of Table I gives the values of γ calculated by means of this relation. The viscosity data given in column VI were determined in this laboratory by Mr. G. Y. Williams using the apparatus described below.[3] The values are so nearly equal to unity that the viscosity correction is practically negligible.

7. The Iodide-Triiodide Equilibrium in Solutions of Hydriodic Acid.

The equilibrium constant, $\frac{[I_2][I^-]}{[I_3^-]} = k_1$, has been determined in a number of ways by several different observers and the results of all these investigations have been recently subjected to a careful criticism by Bray and MacKay[4] in connection with a further experimental study of this equilibrium. They found that in solutions of potassium iodide saturated with iodine the value of k_1 decreased from 1.53 to 1.31 between 0 and 0.1 normal KI, but that in a dilute potassium iodide solution k_1 was practically constant with respect to variations in the concentration of I_2. For the purposes of the present investigation it is necessary to know the value of k_1 quite accurately and to know how it behaves with respect to variations in the concentration of HI in the solution. It seemed desirable, therefore, to determin the value of this constant in hydriodic acid solutions at those concentrations actually employed in the experiments on the arsenious acid-iodine equilibrium. By measuring the conductances of the solutions in these experiments, an opportunity would also be afforded for testing the assumption that HI and HI_3 are ionized to the same degree in solutions of the same total ion concentration.

The following experiments were accordingly made: Solutions of iodine in hydrodic acid of different concentrations were rotated in the thermostat at 25° in contact with a carbon tetrachloride layer until equilibrium was established. The two layers were then drawn off and analyzed. The I_2 in the carbon tetrachloride layer was determined by titration with standard thiosulfate and that in the water layer was calculated by means of the partition constant. A portion of the water layer was then shaken with successive portions of carbon tetrachloride until it was colorless and

[1] Bray and MacKay, *J. Am. Chem. Soc.*, **32**, 921 (1910).
[2] Cf. equation 11, *Ibid.*, **33**, 1471 (1911).
[3] *Ibid.*, **35**, 737 (1913).
[4] Bray and MacKay, *Ibid.*, **32**, 914 (1910).

these carbon tetrachloride solutions were then titrated with the standard thiosulfate solution. In a second portion of the water layer the *total* iodine was then determined by Bray's permanganate method.[1]

TABLE II.—THE IODIDE TRIIODIDE EQUILIBRIUM IN SOLUTIONS OF HI AT 25°. DATA AND RESULTS. CONCENTRATIONS, [ ], IN FORMULA WEIGHTS PER LITER.

$$\frac{[\Sigma HI][I_2]}{[\Sigma HI_3]} = k_1. \qquad \gamma_{HI + HI_3} = \frac{L \cdot 10^3}{[\Sigma HI]\,440 + [\Sigma HI_3]\,405}.$$

I. No.	II. $[\Sigma HI] \cdot 10^3$.	III. $[\Sigma HI_3] \cdot 10^3$.	IV. $[I_2] \cdot 10^3$.	V. $k_1 \cdot 10^3$.	VI. $L \cdot 10^5$.	VII. γ_{HI+HI_3}.	VIII. ΣC_i.	IX. γ_{HI}.
1	80.1	82.1	1.32	1.29	6195	0.906	0.1471	0.891
2	55.4	56.7	1.32	1.29	4250	0.900	0.1009	0.903
3	67.62	37.08	0.720	1.31	3973	0.888	0.0930	0.906
4	64.96	33.36	0.684	1.33	3761	0.895	0.0879	0.908
5	87.62	4.636	0.0694	1.31	3652	0.896	0.0826	0.909
6	72.95	1.349	0.0241	1.30	2982	0.914	0.0678	0.915
7	57.15	0.904	0.0202	1.28	2342	0.921	0.0533	0.922
				Mean 1.30				
				a. d. 0.015				

The results are shown in Table II. Columns II, III, and IV give the concentrations of *total* HI, *total* HI_3, and I_2 respectively. Column V gives the values of the constant, $\frac{[\Sigma HI][I_2]}{[\Sigma HI_3]} = k_1$. Column VI gives the measured values of the specific conductances L of the solutions and column VII the values of γ, the degree of ionization of the HI and the HI_3 in the solution, calculated on the assumption that both acids are ionized to the same degree. These values were computed by means of the relation

$$\gamma = \frac{L \cdot 10^3}{[\Sigma HI]\Lambda_{\infty HI} + [\Sigma HI_3]\Lambda_{\infty HI_3}}. \qquad (17)$$

For $\Lambda_{\infty HI}$ the value 440 was employed. For $\Lambda_{\infty HI_3}$ the value $\Lambda_{\infty HI_3} = \Lambda_{I^-} + \Lambda_{I_3^-} = 440 - 76 + 41 = 405$ was employed, the value $\Lambda_{I_3^-} = 41$ being that determined by Bray and MacKay.

Column VIII shows the values of the total-ion concentration $[\Sigma C_i] = \gamma([\Sigma HI] + [\Sigma HI_3])$, and column IX shows the values of γ_{HI} for solutions of HI having the same total-ion concentration. The values of γ_{HI} were interpolated from a γ-γC curve drawn from the data given in Table I. From the values of k_1 shown in column V it is evident that for ion concentrations between 0.15 and 0.05 N, k_1 is a constant and equal to $1.30 \cdot 10^{-3}$, with an average deviation for the seven experiments of only 0.015 or 1%. This agrees, within the experimental error, with the results obtained by Jakowkin[2] who made a similar series of experiments with HI using CS_2 as the second phase. His values for k_1 vary between 1.30 and 1.35 with an average of $1.32 \cdot 10^{-3}$.

[1] Bray, *J. Am. Chem. Soc.*, **32**, 1193 (1910).

[2] *Z. physik. Chem.*, **20**, 21 (1896).

Moreover, a comparison of the figures in columns VII and IX shows that the average deviation of γ for the mixture from γ for pure HI solutions at the same total-ion concentration is only 0.8% which must be considered as within the experimental error, since the method of computing γ for the mixture neglects the varying influence of the viscosities of the different mixtures. This agreement supports strongly the assumption that the two acids HI and HI_3 are ionized to the same degree in solutions of the same total-ion concentration. Bray and MacKay found the same to be true for the two salts KI and KI_3.

8. The Ionization Constant of Arsenic Acid.

Walden[1] has measured the conductance of solutions of arsenic acid, and of mono-sodium and mono-potassium arsenates at 25°. By plotting values of $(C\gamma)^n$ against those of $1/\Lambda$, using $n = 0.45$ for the sodium salt and $n = 0.50$ for the potassium salt, the value $\Lambda_o = 86.5$ is found for the sodium salt and the value $\Lambda_o = 112$ for the potassium salt, both values being expressed in reciprocal ohms. By subtracting from these two values the equivalent conductance of the sodium ion 51.2, and that of the potassium ion 74.8, respectively, the two values 35.2 and 37, respectively, are obtained for the equivalent conductance of the $H_2AsO_4^-$ ion. The value $\Lambda_{H_2AsO_4^-} = 36$[2] was adopted, and may be in error by one or two units, owing to hydrolysis of the salts, especially at the lower concentrations, but it is sufficiently accurate for the present purpose. Then if the equivalent conductance of the hydrogen ion is taken as 361, Λ_o for arsenic acid is 397.

The ionization constant of arsenic acid calculated from Walden's conductance data by use of the formula $k_{As'} = \dfrac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)}$ is then 4.45×10^{-3} in the most dilute solution, 0.002 n, where $C_i = 0.0015$ and it increases with increasing ion concentration. In order to determin the ionization constant at the ion concentrations used in the equilibrium measurements, the conductances of several hydrochloric acid solutions were measured, and then to the same solutions known amounts of arsenic acid were added and the conductances redetermined. The concentrations of the various molecular constituents of the mixture were then calculated by means of the relations

$$[H_2AsO_4^-] = \frac{10^3.(L' - L)}{\Lambda_{H^+} + \Lambda_{H_2AsO_4^-}} \qquad (18)$$

$$[H^+] = \frac{10^3.L}{\Lambda_{H^+} + \Lambda_{Cl^-}} + [H_2AsO_4^-], \qquad (19)$$

and

$$[H_3AsO_4] = [\Sigma As] - [H_2AsO_4^-], \qquad (20)$$

[1] *Z. physik. Chem.*, **2**, 52 (1888).

[2] Cf. Luther, *Z. Elektrochem.*, **13**, 297 (1907).

L being the specific conductance of the pure hydrochloric acid and L′ that of the mixture. The results are shown in Table III. The last column of the table shows the values of $k_{As'} = \frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]}$, which evidently decreases regularly with decreasing ion concentration. In order to express

TABLE III.—CONDUCTANCE AND IONIZATION OF H_3AsO_4 IN SOLUTIONS OF HCl.

$$\frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]} = k_{As'}.$$

I. $[\Sigma HCl] \cdot 10^3$.	II. L.	III. L′.	IV. $[H_2AsO_4^-] \cdot 10^3$.	V. $[H^+] \cdot 10^3$.	VI. $[H_3AsO_4] \cdot 10^3$.	VII. $k_{As'} \cdot 10^3$.
126.8	0.04903	0.05004	2.52	114.8	50.4	5.75
101.1	0.03952	0.04071	2.99	93.6	50.0	5.60
50.57	0.02022	0.02219	4.99	51.4	47.8	5.30

this "constant" as a function of the ion concentration C_i, the Kraus equation[1] $k_{As'} = k + DC_i^m$ was employed, giving

$$\frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]} = 4.32 + 4C_i^{1/2}, \qquad (21)$$

which holds for the range of total-ion concentrations involved in the final equilibrium measurements.

9. The Ionization Constants of Arsenious Acid.

Arsenious acid is a very weak acid having an ionization constant[2] of 2.10^{-8} and hence in the presence of a strong acid its ionization as an acid is quite negligible. Owing to its amphoteric nature it can, however, function as a base in a strongly acid solution. This is shown by the decrease in the conductance of hydriodic or of hydrochloric acid which occurs when arsenious acid is added to the solution. Its ionization as a base may be expressed by the reaction

$$H_3AsO_3 = AsO^+ + OH^- + H_2O$$

giving the ionization constant

$$\frac{[AsO^+][OH^-]}{[H_3AsO_3]} = k_{As}, \qquad (22)$$

where H_3AsO_3 is understood to mean the sum of the concentrations of all the unionized forms in which the substance exists in the solution.[3]

In order to determin the constant k_{As}, the following experiment was resorted to. The specific conductance L of a 0.1 N hydrochloric acid solution at 25° was found to be 0.03952. After dissolving 0.0404 formula

[1] See Bray, *Trans. Amer. Electrochem. Soc.*, 21, 144 (1912); Noyes and Falk, *J. Am. Chem. Soc.*, 34, 484 (1912).

[2] Zawidski, *Ber.*, 36, 1433 (1903).

[3] Thus the following forms may exist: H_3AsO_3, $As(OH)_3$, $AsO(OH)$, AsO_2H, etc. The freezing-point measurements of Raoult (*Ann. chim. phys.* [6] 2, 81; 11, 288; 15, 375) and the boiling-point measurements of Biltz (*Z. physik. Chem.* 19, 422 (1896)) and of Zawidski (*loc. cit.*) 36, 1429 (1903)) show that no polymerization occurs.

weights of $^1/_2$ As_2O_3 in a liter of this solution the specific conductance was found to be L′ = 0.03886. We have, therefore,

$$[AsO^+] = \frac{10^3.(L - L')}{\Lambda_{H^+} + \Lambda_{AsO^+}}, \qquad (23)$$

$$[OH^-] = \frac{(\Lambda_{H^+} + \Lambda_{Cl^-})10^{-14}}{10^3.L}, \qquad (24)$$

and

$$k_{As} = \frac{10^{-14}(\Lambda_{H^+} + \Lambda_{Cl^-})}{0.0494(\Lambda_{H^+} - \Lambda_{AsO^+})}\left(\frac{L - L'}{L}\right). \qquad (25)$$

From Zawidski's conductance measurements on solutions of NaH_2AsO_3, the conductance of the $H_2AsO_3^-$ (or AsO_2^-) ion is found to be 31.5. Reasoning from analogy we may, therefore, conclude that the conductance of the AsO^+ ion will be about 40 reciprocal ohms. Equation (25) gives, therefore, $k_{As} = 0.13.10^{-14}$ which agrees well with the value $0.18.10^{-14}$ which can be calculated from similar measurements carried out by Zawidski, who used hydriodic acid in place of hydrochloric.

10. The Measurement of the Arsenious Acid-Iodine Equilibrium.

Experimental Procedure: Experiments 1-6.—The equilibrium vessel consisted of a two-liter, glass-stoppered bottle of resistance-glass, which was filled in the following manner: The air was first displaced by a rapid current of nitrogen and then the desired amounts of solid iodine, carbon tetrachloride, and arsenious acid solution were introduced, the first by allowing it to fall in a fine powder through the nitrogen, and the two liquids from their respective stock bottles by means of nitrogen pressure. The bottle was then stoppered and sealed with Khotinsky cement. If the equilibrium was to be approached from a higher temperature, the mixture was allowed to stand at room temperature (about 30°) for two days before being placed in the thermostat, but if from a lower temperature, it stood in the ice chest for two days. When the bottle had been rotated in the thermostat for 24 hours at 25°, it was opened and the contents analyzed, preliminary experiments having shown that equilibrium was reached within twenty-four hours, which agrees with the observations of Roebuck. The water layer was removed by means of a pipet, and transferred to a weight buret,[1] from which portions were weighed out for analysis. In order to obtain samples of the carbon tetrachloride layer, a pipet having its lower end sealed together and blown out into a thin bulb was employed. This was lowered into the carbon tetrachloride, and the bulb broken against the bottom of the bottle. The samples were transferred to weighed flasks and weighed. The densities both of the water layer and the carbon tetrachloride layer were measured in order that the concentration by volume might be calculated. The iodine in the carbon tetrachloride was

[1] Fig., *J. Am. Chem. Soc.*, **30**, 40 (1908).

determined by titration with tenth normal thiosulfate. In some experiments the free iodine in the water layer was reduced to hydriodic acid by sodium sulfite. The solution was then diluted to about hundredth normal, made acid with nitric acid, and the hydriodic acid precipitated by very dilute silver nitrate. In other experiments, the water layer was titrated with tenth normal arsenious acid, after the addition of sufficient disodium phosphate to make it just neutral when the end point was reached.[1] By either method the total iodine in the aqueous layer can evidently be calculated.

The concentrations of the various molecular species present were then computed by the methods outlined in section 3. The results are shown in Table IV. In order to illustrate the calculation of these values from the experimental data, the calculation for experiment number 1 is here given in detail. The analytical data are $[\Sigma As] = 0.10128$ gram atom per liter, $[\Sigma I] = 0.18568$ gram atom per liter, and $[I_2]$ in the carbon tetrachloride layer = 0.005325 mol per liter.

Reference to figure on p. 689 shows that at this concentration of iodine the partition constant is 85.1, hence $[I_2]$ in the water layer $= \frac{0.005325}{85.1} = 0.0000625$. Preliminary calculation showed the total ion concentration to be 0.153, and from the γ-γC-curve prepared from the data given in Table I, the degree of dissociation of HI and HI_3 in this solution is found to be 0.885. Substituting these values in equation (6) we obtain

$$\frac{1}{0.885}[I^-] + \frac{3}{0.885} \cdot \frac{0.0000625[I^-]}{1.30 \times 10^{-3}} = 0.1857 - 2 \times 0.00006 \quad (26)$$

which, when solved, gives $[I^-] = 0.1433$. Then, on substituting this value in equations (7), (8), and (9) the following results are obtained:

$$[HI] = \frac{1 - 0.885}{0.885} \times 0.1433 = 0.01866, \quad (27)$$

$$[I_3^-] = \frac{0.0000625 \times 0.1438}{1.30 \times 10^{-3}} = 0.00690, \quad (28)$$

$$[HI_3] = \frac{1 - 0.885}{0.885} \times 0.00690 = 0.000903. \quad (29)$$

The total arsénic-arsenic concentration is obtained by use of equation (10) as follows:

$$[H_3AsO_4] + [H_2AsO_4^-] = 1/2(0.1438 + 0.0186 + 0.0069 + 0.0009) = 0.08510. \quad (30)$$

Assume as a first approximation that

$$[H^+] = [I^-] + [I_3^-] \quad (31)$$

$$= (0.1433 + 0.0069) = 0.1502. \quad (32)$$

[1] Washburn, *loc. cit.*; *J. Am. Chem. Soc.*, **30**, 31 (1908).

Now, $k_{As'}$, the dissociation constant of arsenic acid, $= (4.32 + 4(0.153)^{0.5}) \times 10^{-3}$.

Hence,

$$[H_2AsO_4^-] = \frac{5.87 \times 10^{-3} \times 0.08510}{0.1502} = 0.00333. \qquad (33)$$

For a second approximation,

$$[H^+] = [I^-] + [I_3^-] + [H_2AsO_4^-]$$
$$= 0.1433 + 0.0069 + 0.0033 = 0.1535 \qquad (34)$$

and

$$[H_2AsO_4^-] = \frac{5.87 \times 10^{-3} \times 0.08177}{0.1535} = 0.00313. \qquad (35)$$

A third approximation gives practically the same value, 0.00314, for the concentration of the arsenate ion. Hence, $[H_3AsO_4] = 0.08197$ and $[H^+] = 0.1533$.

By substituting the above values of the arsenic acid and the arsenate ion concentrations in equation (3), we find that

$$[H_3AsO_3] + [AsO^+] = 0.10128 - 0.08510 = 0.01618. \qquad (36)$$

Then from equation (12) we obtain

$$[AsO^+] = 0.13 \times 0.01618 \times 0.1533 = 0.00032. \qquad (37)$$

Hence,

$$[H_3AsO_3] = 0.01586, \qquad (38)$$

and

$$K_C = \frac{(0.08197)(0.1533)^2(0.1433)^3}{(0.01586)(0.00690)} = 5.20 \times 10^{-2}. \qquad (39)$$

Experimental Procedure: Experiment 7.—Experiment 7 was undertaken for the purpose of ascertaining the effect upon the equilibrium constant, of a large variation in the value of $[H^+]$ in the solution. The only practicable method by which this variation can be effected is by the addition of an iodide to the equilibrium mixture. Experiment 7 was, therefore, carried out as follows: 116 grams of potassium iodide and 30 cc. of a 0.09553 normal iodine solution containing 0.12 formula weights of KI per liter were mixed with 50.97 grams of a 3.530 formal solution of H_3AsO_4 and 30.52 grams of a 0.05870 formal solution of H_3AsO_3 and the whole made up to a volume of 6 liters. This mixture was then shaken in a 10-liter bottle with 1350 cc. of carbon tetrachloride for 24 hours at 25°.

The carbon tetrachloride layer was found on analysis to contain $1.49.10^{-4}$ formula weights of I_2 per liter. From this figure and the original composition of the mixture the values shown in the table are readily calculated. The concentration of potassium ion in this solution when equilibrium was attained was 0.1021 equivalents per liter.

The Conductance of the Equilibrium Mixture.—By measuring the specific conductances of the equilibrium mixtures a check can be secured upon the

experimental results and the calculations. Such measurements were made in all but the first two experiments. Column 15 in Table IV shows

TABLE IV. — ARSENIOUS ACID $\rightleftharpoons$ IODINE EQUILIBRIUM AT 25°. DATA AND RESULTS

CONCENTRATIONS, [ ], IN FORMULA WEIGHTS PER LITER-AT-25°.

$$\frac{[H_3AsO_4]\,.\,[H^+]^2\,.\,[I^-]^3}{[H_3AsO_3]\,.\,[I_3^-]} = K_c.$$

1912 Atomic Weights.

Exp. No.	1. Density 25°/25°.	2. $[\Sigma I]\,.\,10^3$.	3. $[\Sigma As]\,.\,10^3$.	4. $[I_2]\,.\,10^3$.	5. $C_i\,.\,10^3$.	6. $r_{HI} = r_{HI_3}$
1*	1.0232	185.68	101.28	0.0625	154	0.884
2	1.0250	206.86	101.21	0.0943	160	0.882
3*	1.0140	90.59	51.98	0.00727	84	0.906
4*	1.0155	107.34	49.37	0.0720	90	0.904
5*	1.0148	102.48	49.35	0.0446	90	0.904
6	1.0144	101.40	49.34	0.0394	89	0.904
7	....	....	....	0.0175	111.7	0.862

Exp. No.	7. $[I^-].10^3$.	8. $[I_3^-].10^3$.	9. $[H^+].10^3$.	10. $[AsO^+].10^3$.	11. $[H_3AsO_3]\,.10^3$.	12. $[H_2AsO_4^-].10^3$.
1*	143.3	6.904	153.3	0.32	15.86	3.14
2	146.1	10.84	160.1	0.25	12.00	3.18
3*	80.79	0.442	83.97	0.080	7.07	2.74
4*	83.12	4.599	90.51	0.010	0.832	2.79
5*	83.97	2.878	89.62	0.015	1.301	2.78
6	84.02	2.548	89.36	0.017	1.437	2.79
7	101.00	0.136	9.63[1]	0.0000	0.253	10.60

Exp. No.	13. $[H_3AsO_4].10^3$.	14. $K_c.10^2$.	15. $L_{obs.}$	16. $L_{calc.}$	17. $L_{calc.}-L_{obs.}$	18. $C^{1/2}$.
1*	81.97	5.20	.....	.....	.....	0.392
2	85.78	5.64	.....	.....	.....	0.400
3*	44.83	5.32	0.03632	0.03657	0.00025	0.290
4*	45.73	5.62	0.03905	0.03926	0.00021	0.300
5*	45.25	5.75	0.03870	0.03900	0.00030	0.300
6	45.09	5.84	0.03847	0.03882	0.00036	0.298
7	19.60	5.43	0.01904	0.01918	0.00014	0.333
	Mean	5.54		Mean	0.00025 = 0.6%.	0.330 ±0.038
	a. d.	0.19 = 3.5%				
	Max. d.	0.34 = 6%				
	P. E.	0.06 = 1.2%				

the measured values of the specific conductances L of the various equilibrium mixtures, and column 16 the values L′ calculated from the corresponding ion concentrations shown in columns 7, 8, 9 and 12, by means of the usual equation

$$10^3.L' = [H^+]\Lambda_{H^+} + [I^-]\Lambda_{I^-} + [I_3^-]\Lambda_{I_3^-} + [H_2AsO_4^-]\Lambda_{H_2AsO_4^-} + [K^+]\Lambda_{K^+} \qquad (40)$$

* Indicates equilibrium approached from higher temperature.

[1] $[K^+]$ in this experiment was 0.1021.

employing the values $\Lambda_{H^+} = 361$, $\Lambda_{I^-} = 76.5$, $\Lambda_{I_3^-} = 41$, $\Lambda_{H_2AsO_4^-} = 36$ and $\Lambda_{K^+} = 74.3$.

It will be noticed that the calculated and observed specific conductances differ on the average by only 0.6%, which is better agreement than could justly be expected, since the relative viscosities of some of the mixtures were as large as 1.03 and the effect of this factor is only partially allowed for in the above method of obtaining the calculated values.

11. The Equilibrium Constant and the Mass Action Law.

The values of

$$K_C{}^1 = \frac{[H_3AsO_4][H^+]^2[I^-]^3}{[H_3AsO_3][I_3^-]}$$

are given in column 14 of Table IV.

It will be noted that the mean value of this constant is $5.5.10^{-2}$, with an *average deviation* from the mean for the seven experiments, of only 3.5% and a *maximum deviation* of only 6%, the "probable error" being 1.2%. Moreover, these small deviations are evidently irregular and without significance. We must, therefore, conclude that under the conditions of the above experiments, this *equilibrium obeys the law of mass action within the small experimental error of 4%.*

To appreciate the full significance of this result, the ranges of variation undergone by the concentrations of the different substances in the series of experiments should be carefully noted. They are as follows: $[I_2]$, *from 0.000007 to 0.00009 molal or 13-fold;* $[I^-]$, *from 0.08 to 0.14 normal or nearly 2-fold;* $[I_3^-]$, *from 0.00014 to 0.011 or 80-fold;* $[H^+]$, *from 0.000 to 0.16 or more than 16 fold;* $[H_3AsO_3]$, *from 0.00025 to 0.016 or more than 60-fold;* $[H_3AsO_4]$, *from 0.02 to 0.086 or more than 4-fold.* The smallest concentration range covered by any of these substances is that for the iodide ion, about 2-fold, but since the concentration of this substance appears as the cube in the expression for the equilibrium constant, the effect of this variation is increased 3-fold and thus becomes comparable with the others. The case of the hydrogen ion is especially interesting for since its concentration appears as the square in the expression for the equilibrium constant, its large variation of 16-fold might be expected to show up any abnormality in its behavior by a corresponding effect upon the equilibrium constant.

[1] If the concentrations of the molecular species concerned in the equilibrium were expressed in terms of mol fractions, *x*, instead of mols per liter, the corresponding constant K_x would be related to the constant K_c in the following manner,

$$K_c = K_x \cdot n_{H_2O} \cdot (\Sigma n)^3$$

where n_{H_2O} is the number of mols of H_2O and (Σn) the total number of mols of all the molecular species contained in one liter of the solution. If k_x is a true constant, then the same will be true of K_c except for variations in the factor $n_{H_2O}(\Sigma n)^3$. For the range of concentrations included in the present investigation this factor does not vary by more than two per cent. of itself and hence the constant K_c is a sufficiently satisfactory basis for expressing the results.

No such effect is noticeable, however, and, if present, must be almost exactly compensated by some other influence.

12. The Heat of the Reaction.

The heat of the reaction between arsenious acid and iodine in dilute aqueous solution may be calculated from the following thermochemical equations:

$H_3AsO_3(Aq) + O(Aq)$	$= H_3AsO_4(Aq)$	$+ 39{,}205$	(1)
$H_2O(liq)$	$= H_2(gas) + O(gas)$	$- 68{,}303$	(2)
$O(gas)$	$= O(Aq)$	$+ 1{,}487$	(3)
$H_2(gas) + I_2(solid) + (Aq)$	$= 2H^+ + 2I^-$	$+ 26{,}400$	(4)
I_3^-	$= I_2(Aq) + I^-$	$- 3{,}820$	(5)
$I_2(Aq)$	$= I_2(solid)$	$+ 6{,}390$	(6)

$$H_3AsO_3(Aq) + H_2O + I_3^- = H_3AsO_4(Aq) + 2H^+ + 3I^- + 1360 \text{ cal.}$$

In the case of the first, second and fourth of the above reactions the values given are taken from Thomsen ("Thermochemische Untersuchungen"). The heat of solution of oxygen (reaction 3) and that of iodine (reaction 6) were calculated from the solubilities of the substances at two different temperatures by means of the equation

$$\Delta H = R \log_e \frac{S_2}{S_1} \div \left(\frac{1}{T_1} - \frac{1}{T_2}\right). \qquad (41)$$

In the case of oxygen Winkler[1] and Bohn and Boch[1] have determined the solubility at various temperatures and from their data the values $S_{20^\circ} = 0.004440$ and $S_{30^\circ} = 0.003744$ were computed for the solubility of oxygen under a pressure of one atmosphere. These values give $\Delta H = 2974$ as the heat of solution (heat absorbed) per mol. In the case of iodine, Sammet[2] found the values $S_{25^\circ} = 0.001342$ and $S_{40^\circ} = 0.004160$ mol per liter. These values give $\Delta H = 6390$ as the mean molecular heat of solution of iodine between these two temperatures.

In order to obtain the heat effect of reaction 5 above, the values of the logarithm of the equilibrium constant $\frac{[I^-][I_2]}{[I_3^-]} = k$, obtained by different investigators[3] were plotted against the corresponding temperatures and the values $k_0 = 0.735 \cdot 10^{-3}$ and $k_{25^\circ} = 1.34 \cdot 10^{-3}$ obtained by interpolation. In preparing this plot the values of k employed at each temperature were those for an ion concentration of about 0.1 equivalent per liter. By means of the van't Hoff equation the value $\Delta H = 3820$ cal. was then calculated.

[1] Landolt-Bornstein-Meyerhoffer, *Tabellen*, p. 599 (3rd Ed.).

[2] *Loc. cit.*

[3] Fedotieff, *Z. anorg. Chem.*, 69, 32 (1910); Jakowkin, *Z. physik. Chem.*, 13, 541 (1894); 20, 19 (1896); Dawson, *J. Chem. Soc.*, 79, 238 (1901); *Z. physik. Chem.*, 56, 605 (1906); Bray and Mackay, *loc. cit.*

The value $\Delta H = -1360$ cal. for the reaction between arsenious acid and iodine, obtained from this set of thermochemical equations, corresponds to a multiplication of the equilibrium constant by the factor 1.1 for a rise of 10°. This is in good agreement with the observations of Roebuck[1] who found values of this factor varying between 1.1 and 1.3 for the "constant" computed by him (cf. Sec. 2).

By means of the van't Hoff equation we obtain the general expression

$$\log_{10} K_c = -1.3495 + 0.00372\, t \qquad (42)$$

from which the equilibrium constant of the arsenious acid-iodine equilibrium may be computed for any temperature, t (Centigrade).

13. The Free Energy of the Reaction.

Definition of the Term "Free Energy."—As a measure of chemical affinity the thermodynamic potential at constant pressure (Gibbs' ζ-function) is a more convenient function to employ than is the maximum work of the reaction, which under the name of "free energy" was first employed for this purpose by Helmholtz. For this reason and also because of the confusion which has arisen in connection with the use of these two functions, G. N. Lewis has recently[2] proposed to transfer the name free energy to the former function and to employ this function (represented by the letter F) exclusively as a measure of chemical affinity. The *increase* in free energy which accompanies any process would then be represented by the symbol ΔF and the *partial free energy* of any molecular species in a mixture by the symbol $\bar{F}$. The latter quantity corresponds to the molecular thermodynamic potential and is the quantity represented by μ in our equation (52) above.

The value of $\Delta F°$ for any chemical reaction taking place in a medium of constant thermodynamic environment is given by the expression

$$\Delta F° = RT \log_e K \qquad (43)$$

where K is the equilibrium constant for the particular thermodynamic environment in question and the reaction is considered as taking place between the reacting substances at such initial concentrations that their activities in this particular thermodynamic environment are each equal to unity and ending with the products of the reaction at such final concentrations that their activities are also each equal to unity. It is clear, therefore, that the free energy of a chemical reaction depends upon the medium in which the reaction occurs. Thus in the case of the arsenious acid-iodine equilibrium we might calculate the value of $\Delta F°$ for this reaction in an infinitly dilute aqueous solution or we might calculate its value in an aqueous solution having a constant ion concentration of, say, 0.1 equivalent per liter. We shall consider here only the latter case.

[1] *Loc. cit.*

[2] Lewis, *J. Am. Chem. Soc.*, **35**, 14 (1913).

ΔF° for the Arsenious Acid-Iodine Equilibrium.—Putting $K_c = 5.54 \cdot 10^{-2}$ in equation (69) above we have

$$\Delta F^\circ_{25^\circ} = RT \log_e K = -7170 \text{ joules} \qquad (44)$$

or

$$H_3AsO_3 + H_2O + I_3^- = H_3AsO_4 + 2H^+ + 3I^-; \quad \Delta F^\circ_{25^\circ} = -7170 \text{ joules}$$

in any aqueous solution having an ion concentration not far from 0.1 equivalent per liter.

The general expression for ΔF° for this reaction under the conditions stated, as obtained from equations (68) and (70), is

$$-\Delta F^\circ = RT \log_e k_c = 5690 + 5.42T \text{ (joules)} \qquad (45)$$

which holds for the range of temperatures within which the heat of the reaction may be assumed to be constant and equal to 1360 cal.

14. The Potential of the "Normal" Arsenic Electrode.

Consider the wholly hypothetical cell

$$\begin{array}{rc|c|c|c|l} & & H_3AsO_4 & & I_3^- & \\ -\,Pt & | & H_3AsO_3 & \longrightarrow & I^- & |\,Pt\,- \\ & & H^+ & \longleftarrow & A\ B & \\ & & A\ B & & & \end{array}$$

prepared as follows: Solutions of the salt AB are prepared of such ion concentrations that when the cell is completed the thermodynamic environment (which can be controlled by means of AB) on both sides of the cell shall be substantially that which prevails in the equilibrium mixtures described by Table IV, that is, an ion concentration of about 0.1 equivalent per liter must exist on both sides of the cell. In the left half the molecular species H_3AsO_4, H_3AsO_3 and H^+ are present at such concentrations that the activity of each is equal to unity and in the right half the molecular species I_3^- and I^- are present, also at such concentrations that the activity of each is equal to unity.

The potential **E** of this cell will be

$$E = \frac{\Delta F^\circ}{2 \cdot 96{,}500} = \frac{7170}{2 \cdot 96{,}500} = 0.037 \text{ volt.} \qquad (46)$$

If we call the separate electrode potentials, the potential of the "normal" arsenic electrode (E°_{As}) and the potential of the "normal" iodine electrode (E°_I), respectively, we have

$$E^\circ_{As} + E^\circ_I = 0.037. \qquad (47)$$

The potential of the normal iodine electrode as customarily defined is +0.256 volt when measured against the normal calomel electrode. If this is also the potential of the "normal" iodine electrode as defined above —and it will not be far from it—we have

$$E^{\circ}_{As} = 0.037 + 0.256 = 0.293 \text{ volt} \qquad (74)$$

as the potential of the "normal" arsenic electrode.[1]

Loimaranta[2] attempted to measure directly the potential of the arsenic electrode by using a platinum electrode dipping into a mixture of arsenious, arsenic, and sulfuric acids to which a trace of potassium iodide had been added to act as a carrier and to make the electrode reversible. In a discussion of these measurements, Luther[3] pointed out that no proof was given that the electrode was truly reversible under these conditions and the action of the oxygen of the air upon the iodide in the presence of the acid would have been a source of considerable error. From three of Loimaranta's experiments Luther calculated the following values for the potential of the "normal" arsenic electrode, 0.322, 0.339, and 0.333. The mean of these, 0.33 volts, is 4 centivolts higher than the value calculated above from our equilibrium constant.

15. Summary and Conclusions.

Concentrations in formula weights per liter.

1. At infinit dilution and 25° the distribution constant for the partition of I_2 between H_2O and CCl_4 is $\frac{[I_2]_{CCl_4}}{[I_2]_{H_2O}} = 85.0$.

2. The following equivalent conductances were determined for HI solutions at 25°, at the equivalent concentrations indicated: 0.15 N, 389.5; 0.1 N, 395.6; 0.08 N, 398.5; 0.05 N, 404.3. They are all more than 2% higher than Ostwald's values.

3. The value of the constant $\frac{[I_2][I^-]}{[I_3^-]}$ at 25° in solutions of HI is (1.30 ± 0.015).10^{-3} for total-ion concentrations lying between 0.05 and 0.15 equivalents per liter. In a mixture of HI and HI_3 both acids are ionized to the same degree.

4. The value of Λ_0 for the $H_2AsO_4^-$ ion at 25° is 36 reciprocal ohms. The ionization of H_3AsO_4 at 25° can be expressed by the relation $\frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]} = 10^{-3}.(4.32 + 4C_i^{1/2})$, where C_i is the total-ion concentration in the solution.

5. The basic ionization constant of arsenious acid at 25° is $\frac{[AsO^+][OH^-]}{[H_3AsO_3]} = 0.15 \cdot 10^{-14}$ in a solution having an ion concentration of 0.1 equivalent per liter.

[1] This statement is made subject to the condition mentioned because our usual E. M. F. equations are all derived on the assumption of a constant thermodynamic environment. They need to be revised on the basis of an equation of state which takes into account the change of thermodynamic environment with changing ion concentration.

[2] Loimaranta, *Z. Electrochem.*, **13**, 33 (1907).

[3] Luther, *ibid.*, **13**, 291 (1907).

6. The value of the equilibrium expression

$$\frac{[H_3AsO_4][H^+]^2[I^-]^3}{[H_3AsO_3][I_3^-]} = K_c$$

was determined at 25° by direct measurement, the method employed consisting in bringing together, out of contact with the air, a standard solution of H_3AsO_3 in water and a solution of I_2 in CCl_4. When equilibrium was attained a sample of each liquid phase was removed and its total iodine content determined by analysis. From these data the value of K_c can be calculated with an accuracy of better than 1%. In the seven experiments which were made in this manner the concentrations of the different molecular species taking part in the equilibrium were varied through the following concentration ranges: (I_2) from 0.000007 to 0.00009 or *13*-fold; (I^-) from 0.08 to 0.14 or nearly *2*-fold; (I_3^-) from 0.00014 to 0.011 or *80*-fold; (H^+) from 0.0096 to 0.16 or more than *16* fold; (H_3AsO_3) from 0.00025 to 0.016 or more than *60*-fold; and (H_3AsO_4) from 0.02 to 0.086 or more than *4*-fold. In spite of these large variations of concentration, the value of K_c was found to be constant within the experimental error, the mean for the seven experiments being $5.5.10^{-2}$ with an average deviation of only 3.5% and a maximum deviation of only 6%. The apparent close adherence to the requirements of the mass-action law shown by this reaction, involving as it does three species of unionized molecules and three species of ions, the concentrations of two of the latter appearing as the second and third powers, respectively, in the equilibrium expression, contrasts strongly with the great deviation from the requirements of the mass action law exhibited by the ionization of a strong electrolyte.

7. The heat of the reaction is 1360 cal.

8. The general expression for K_c is

$$\log_{10}K_c = -1.3495 + 0.00372t.$$

9. The "free energy" of the reaction is

$$-\Delta F^\circ = RT \log_e K_c = 5690 + 5.42T \text{ (joules)}$$

for the conditions described in sec. 13.

10. The potential of the "normal" arsenic electrode is 0.293 volt under the conditions explained in sec. 14.

AUTOBIOGRAPHY.

The writer of this thesis received his early education in the public schools of Brockton, Massachusetts, graduating from the high school of that city in 1904. In the fall of the same year, he entered the Worcester Polytechnic Institute at Worcester, Massachusetts, and in 1908, he completed the course in chemistry at that institution, receiving the degree of Bachelor of Science. He went to the University of Illinois in the fall of the same year for further study, having received appointment there to the position of graduate assistant in chemistry. This position he held for three years, and in 1911 was made fellow in chemistry, which position he now holds. During his four years at the University of Illinois the writer has studied for the doctorate, specializing both in physical and organic chemistry. In 1910 he received the degree of Master of Science, having prepared a thesis entitled "The Action of the Haloid Acids on Ethyl Oxomalonate." This was later published in conjunction with Dr. R. S. Curtiss, under whose direction that investigation was carried on, in the *Journal of the American Chemical Society* with the title "Condensations in the Mesoxalic Ester Series." Since that time the writer has been engaged in the research which forms the basis of the accompanying thesis.